Gossamer Superconductivity near Antiferromagnetic Mott Insulator in Layered Organic Conductors

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Layered organic superconductors are on the verge of the Mott insulator. We use Gutzwiller variational method to study a Hubbard model including a spin exchange coupling term. The ground state is found to be a Gossamer superconductor at small on-site Coulomb repulsion U and an antiferromagnetic Mott insulator at large U, separated by a first order phase transition. Our theory is qualitatively consistent with major experiments reported in organic superconductors.

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There has been much interest recently on the novel physics of layered organic superconductor [1, 2, 3, 4, 5]. These compounds share most common physical properties with the high-T_c superconductor but typically with much reduced temperature and energy scales. κ-(BEDT-TTF)$_2$X (X=anion) is a family of the best characterized organic superconductors, where the quasi-2-dimensional (2D) Fermi surface has been observed and a direct first order transition between antiferromagnetic (AFM) insulator and superconductor can be tuned by applied pressure or magnetic fields [6, 7, 8, 9, 10]. The resemblance of its pressure-temperature phase diagram to that of the carrier-density-temperature phase diagram in cuprates and the fact of close proximity between the superconducting (SC) and AFM insulating phases have been taken as evidences for similar mechanisms governing high T_c superconductors. There have been strong evidences that the organic superconductors are at the verge of the Mott insulator [6, 7], exhibiting the pseudogap phenomenon [8]. While an ongoing debate persists as to the precise symmetry of the singlet pairing, more recent NMR [11, 12], angular dependent STM [13] and thermal conductivity measurements in the vortex state [14] indicate a $d_{x^2-y^2}$ symmetry.

The low energy electronic structure of the organic superconductors is well approximated by a 2D Hubbard model at the half filling. Different from the cuprates, organic compounds can be SC at the half filling, which makes t-J model inappropriate to describe its SC state. Most theoretical works so far have taken a weak-coupling approach, in which a Hartree-Fock mean field [15], fluctuation-exchange approximation [16, 17, 18, 19] or random phase approximation method [20] are used. The weak coupling theory gives a phase diagram of the AFM and SC states qualitatively consistent with the experiments. However, the weak coupling theory has difficulties to address the Mott insulator or the pseudogap phenomenon [6, 7, 8]. The transition between SC and AFM has also been investigated by using renormalization group method [21].

Very recently, Laughlin has proposed a Gossamer Hamiltonian of which a partially Gutzwiller projected BCS state is an exact ground state with a tiny superfluid density at the half filling [22]. In that Hamiltonian, the SC state has an instability toward the AFM ordering [23]. Some of the present authors [24, 25] have examined the Gossamer superconductor, the Mott insulator, and the resonating valence bond (RVB) state [26, 27, 28] in strongly correlated electron systems with the hope to unify the superconductivity in cuprates and in organic compounds [29]. In our previous study, we focused on the metallic/SC and insulating nature of the problem and neglected the antiferromagnetism. A related approach was recently taken by Baskaran [30], who introduced a two-species t-J model to describe independent motions of empty sites and doubly occupied sites in an otherwise spin-1/2 background, and discussed the relevance of the model to the organic superconductors.

In this Letter, we use Gutzwiller's variational method to study the interplay between SC and AFM states in a modified Hubbard model in 2D given by Eqn. (1) below. By using a renormalized mean field theory developed early for the t-J model [27], we find that at the half filling the ground state is an AFM Mott insulator at large on-site repulsion U and a Gossamer superconductor at small U, followed by a normal metallic state at further smaller U. The transition between the AFM and SC phases is first order, and there is no co-existence of the two phases at the half filling. The doping dependence of the model at large U is similar to that of the t-J model [26]. Our results are qualitatively consistent with major experiments in organic superconductors.

We consider a modified Hubbard model on a square lattice,

$$H = U\sum_i n_{i\uparrow}n_{i\downarrow} - \sum_{\langle ij\rangle\sigma} t_{ij}(c^\dagger_{i\sigma}c_{j\sigma} + h.c.) + J\sum_{(ij)} \vec{S}_i\cdot\vec{S}_j - \mu\sum_{i\sigma} n_{i\sigma} \quad (1)$$

In the above Hamiltonian, $c_{i\sigma}$ is an annihilation operator of an electron at site i with spin σ, $n_{i\sigma} = c^\dagger_{i\sigma}c_{\imath\sigma}$, and

$U > 0$ is the on-site Coulomb repulsion. The non-zero hopping integrals are $t_{ij} = t$ for the nearest neighbor (n.n.) pairs and $t_{ij} = t'$ for the next n.n. pairs along [1,1] direction. $\vec{S}_i$ is a spin-1/2 operator, and the summation in the spin exchange term is over all the n.n. pairs. We consider $1 > t'/t > 0$, suitable for the organic compounds. This Hamiltonian contains an additional spin exchange term to the standard Hubbard model. In the limit $U \gg t$, the model is reduced to the t-t'-J model. At the half filling, the large U limit of the model is reduced to the AFM Heisenberg model with an AFM ground state at small values of t'/t. At small U, we expect a metallic or a SC ground state. We believe that the model combined with the Gutzwiller trial wavefunction approach, Eqns. (2-3) below is appropriate to study the phase transitions in organic superconductors. Note that the direct application of the Gutzwiller trial wavefunction to the Hubbard model is hardly to obtain the SC pairing because of the non-explicit form of the spin-spin exchange interaction in the Hamiltonian.

To study the phase transition between the AFM and SC states, we consider a partially Gutzwiller projected spin density wave (SDW)-BCS wavefunction [31, 32],

$$|\Psi_{GS}\rangle = \prod_i (1 - \alpha n_{i\uparrow} n_{i\downarrow}) |\Psi_0\rangle \tag{2}$$

$$|\Psi_0\rangle = \prod_{\vec{k}} (u_{\vec{k}} + v_{\vec{k}} d^\dagger_{\vec{k}\uparrow} d^\dagger_{-\vec{k}\downarrow}) \mid 0\rangle \tag{3}$$

where $d_{\vec{k}\sigma} = \cos(\frac{\theta_{\vec{k}}}{2}) c_{\vec{k}\sigma} - \sigma \sin(\frac{\theta_{\vec{k}}}{2}) c_{\vec{k}+\vec{Q},\sigma}$, and $\vec{Q} = (\pi, \pi)$ is the magnetic wave vector. $\prod_i (1 - \alpha n_{i\uparrow} n_{i\downarrow})$ is a Gutzwiller projection operator, which partially projects out the doubly occupied electron states on every lattice site and $0 \le \alpha \le 1$ measures the strength of the projection. Obviously, $\alpha = 0$, and $\alpha = 1$ correspond to a non-projected and a completely projected states, respectively. At $\theta_{\vec{k}} = 0$, we have $d_{\vec{k}\sigma} = c_{\vec{k}\sigma}$, and $\mid \Psi_{GS}\rangle$ is reduced to a partially projected BCS state, which we shall loosely call it Gossamer SC state [22, 24]. In the limit $u_{\vec{k}} v_{\vec{k}} = 0$, $\mid \Psi_0\rangle$ is reduced to a SDW state. The variational parameters are $u_{\vec{k}}, v_{\vec{k}}, \theta_{\vec{k}}$ and α. Such a wavefunction should enable us to study the phase transition between the AFM and SC states. The metallic or insulating phase can be determined by the continuity of the chemical potential.

To carry out the variation, we apply the Gutzwiller approximation to replace the effect of the projection operator by a set of renormalization factors, which are determined by statistical countings [27, 33, 34, 35]. Let $\langle O\rangle$ be the expectation value of the operator O in the state $|\Psi_{GS}\rangle$, and $\langle O\rangle_0$ be that in the state $|\Psi_0\rangle$. The Gutzwiller approximation gives

$$\langle c^\dagger_{i\sigma} c_{j\sigma}\rangle = g^{ij}_t \langle c^\dagger_{i\sigma} c_{j\sigma}\rangle_0, \;\; \langle \vec{S}_i \cdot \vec{S}_j\rangle = g_s \langle \vec{S}_i \cdot \vec{S}_j\rangle_0 \tag{4}$$

where g's are determined by the ratio of the probability of the corresponding physical processes in the projected and unprojected states [27]. We introduce a sublattice magnetization for sublattices A and B,

$$m_0 = \frac{1}{2}\langle n_{A\uparrow} - n_{A\downarrow}\rangle_0 = -\frac{1}{2}\langle n_{B\uparrow} - n_{B\downarrow}\rangle_0 \tag{5}$$

$g's$ are then functions of the electron density n, m_0, and the double occupation number $d = \langle n_{i\uparrow} n_{i\downarrow}\rangle$,

$$\begin{aligned} g_s &= (n - 2d)^2/(n - 2n_+ n_-)^2 \\ g^{ij}_t &= G^i G^j \\ G^A &= g_s^{1/4}[\, s(1 - n_-) + \sqrt{n_- d/n_+}\,] \\ G^B &= g_s^{1/4}[\, s(1 - n_+) + \sqrt{n_+ d/n_-}\,] \end{aligned} \tag{6}$$

In the above equations, $n_\pm = \frac{n}{2} \pm m_0$, and $s = \sqrt{\frac{1-n+d}{(1-n_+)(1-n_-)}}$. The superindex in G refers to the sublattice of the site. Note that there is a one-to-one correspondence between d and α given by,

$$1 - \alpha = s^2 d/g_s n_+ n_- \tag{7}$$

In the absence of the sublattice magnetization, g_t and g_s in Eqn, (6) are reduced to their values in the uniform state [25], which are further reduced, in fully projected case ($\alpha = 1$ or $d = 0$), to the values in the RVB state [27]. Within the Gutzwiller approximation, the variation of the projected state for H in (1) is reduced to the variation of the unprojected state $\mid \Psi_0\rangle$ for a renormalized Hamiltonian H_{eff},

$$\begin{aligned} H_{eff} &= Ud - \sum_{\langle ij\rangle\sigma} g^{ij}_t (c^\dagger_{i\sigma} c_{j\sigma} + h.c.) \\ &\quad + g_s J \sum_{(ij)} \vec{S}_i \cdot \vec{S}_j - \mu \sum_{i\sigma} n_{i\sigma} \end{aligned} \tag{8}$$

To proceed further, we introduce a self-energy χ and a d-wave pairing amplitude Δ,

$$\chi = \sum_\sigma \langle c^\dagger_{i\sigma} c_{i+\hat{x}\sigma}\rangle_0 = \sum_\sigma \langle c^\dagger_{i\sigma} c_{i+\hat{y}\sigma}\rangle_0 \tag{9}$$

$$\Delta = \sum_\sigma \langle \sigma c_{i\sigma} c_{i+\hat{x}\,-\sigma}\rangle_0 = -\sum_\sigma \langle \sigma c_{i\sigma} c_{i+\hat{y}\,-\sigma}\rangle_0 \tag{10}$$

The singlet SC order parameter $\Delta_{SC} \approx g_{SC}\Delta$, with $g_{SC} = (g^{AA}_t + g^{BB}_t)/2$. The pairing amplitude and the SDW state described below defines the variation of $\mid \Psi_0\rangle$. As in the usual SDW variation, we choose $\cos\theta_{\vec{k}} = \epsilon_{\vec{k}}/\xi_{\vec{k}}$, where $\epsilon_{\vec{k}} = -(2tg^{AB}_t + 3Jg_s\chi/4)\gamma_{\vec{k},+}$ is the kinetic energy including a self-energy term of χ, and $\xi_{\vec{k}} = \sqrt{\epsilon^2_{\vec{k}} + \tilde{\Delta}^2_{AF}(\vec{k})}$, with $\tilde{\Delta}_{AF}(\vec{k}) = \Delta_{af} + t'(g^{AA}_t - g^{BB}_t)\zeta_{\vec{k}}$. Δ_{af} is a variational parameter to determine m_0. The second term in $\tilde{\Delta}_{AF}$ arises from a spin-dependent hopping process along the [1,1] direction in H_{eff}. In the above equations, we have denoted $\gamma_{\vec{k},\pm} = \cos k_x \pm \cos k_y$, and $\zeta_{\vec{k}} = \cos(k_x + k_y)$. With the above variational wavefunction, we calculate the expectation value of H_{eff} and find

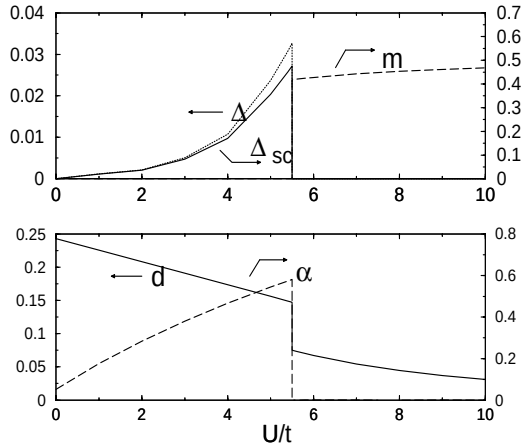

FIG. 1: Pairing amplitude Δ, SC order parameter Δ_{SC}, and AFM order parameter m (top panel), and electron double occupancy number d and the projection parameter α (bottom panel), as functions of U for $J/t = 0.5$ and $t'/t = 0.8$.

the ground state energy,

$$E = Ud - 4g_t t\chi + g_t^{AA}\langle H_{t'}^{+}\rangle_0 + g_t^{BB}\langle H_{t'}^{-}\rangle_0 - (3g_s J/4)(\Delta^2 + \chi^2) - 2Jg_s m_0^2 \quad (11)$$

where m_0, χ, n, and Δ are the solutions of their corresponding self-consistent equations. The two additional variational parameters d and Δ_{af} are to minimalize the ground state energy. Note that $0 \le d \le d_0$, with $d_0 = \langle n_{i\uparrow} n_{i\downarrow}\rangle_0$. In Eqn. (11), $\langle H_{t'}^{\pm}\rangle$ are given by

$$\langle H_{t'}^{\pm}\rangle_0 = -\frac{2t'}{N}\sum_{\vec{k}\in A}\zeta_{\vec{k}}[v_{\vec{k}}^2(1 \mp \sin 2\theta_{\vec{k}}) + v_{\vec{k}+\vec{Q}}^2(1 \pm \sin 2\theta_{\vec{k}})]$$

where the summation of $\vec{k}$ runs over the reduced Brillouin zone, and

$$v_{\vec{k}}^2 = \frac{1}{2}(1 - (\xi_{\vec{k}} - \tilde{\mu})/E_{\vec{k}}^{-}),\ v_{\vec{k}+\vec{Q}}^2 = \frac{1}{2}(1 + (\xi_{\vec{k}} + \tilde{\mu})/E_{\vec{k}}^{+}),$$

with $E_{\vec{k}}^{\mp} = \sqrt{(\xi_{\vec{k}} \mp \tilde{\mu})^2 + \Delta_{\vec{k}}^2}$, and $\Delta_{\vec{k}} = (3/4)Jg_s\Delta\gamma_{\vec{k},-}$, $\tilde{\mu} = \mu + t'(g_t^{AA} + g_t^{BB})\zeta_{\vec{k}}$.

We are now ready to discuss our results. We shall mainly discuss the half filled case. At the half filling, there is a critical U_c to separate a metallic or SC state at a small U from an AFM insulator at a large U, and the transition is first order with no co-existence of the two phases. These features are demonstrated in Fig. 1. There are two regimes in U. At $U < U_c(\sim 5.5\,t)$, $m = 0$ while Δ and Δ_{SC} increase monotonically as U increases. Δ_{SC} is slightly smaller than Δ. This is a SC state without AFM ordering. At $U > U_c$, $\Delta = \Delta_{SC} = 0$, while $m = \sqrt{g_s}m_0$ changes abruptly from zero at $U < U_c$ to a saturated value of 0.45. We have calculated the chemical potential around the half filling and found it is discontinuous in the AFM state so that it is an insulator. As we can see from the bottom panel of Fig. 1, as U increases, d decreases with a sudden drop at U_c indicating

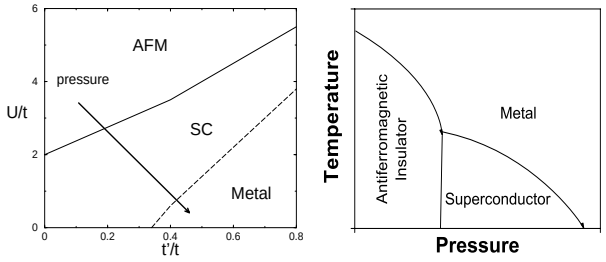

FIG. 2: Left panel: phase diagram of t' v.s. U for $J/t = 0.5$ at the half filling. The arrow indicates the flow of the parameters under the pressure. Right panel: schematic phase diagram of organic superconductors.

the electron's localization in the insulating phase, and α increases to its maximum in the SC phase followed by a discontinuous drop to zero at $U = U_c$. The latter indicates the absence of the projection in the AFM phase so that we have $m = m_0$ [36]. We have also calculated these quantities with different values of J/t and t'/t and the results are qualitatively similar except that Δ becomes very tiny at smaller J/t. Our results are consistent with major experiments in organic superconductors. As shown in the pressure experiments [7], the phase transition is first order and the phase boundary between the AFM and SC states merges with the phase boundary between the insulating and metallic states. In our theory, the AFM state is always a Mott insulator. Recent NMR experiments [6, 8] show the proximity of pseudogapped superconductor and a commensurate AFM ordering with a finite moment of $0.4\mu_B$ (or $0.26\mu_B$) for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl or Br at low temperatures, which suggests that the magnetic ordering is driven by electron's strong correlation rather than by the Fermi surface nesting. In the Gossamer SC state, the quasiparticle energy is governed by Δ [25, 26, 27], which is larger than the SC order parameter, implying a pseudogap phase [37]. The small difference between Δ_{SC} and Δ in our theory is partly due to the phenomenological model we use, which more favors AFM state than the Hubbard model does at moderate or large U. We expect the phase boundary in a more accurate theory will be shifted to the larger U and Δ_{SC}/Δ will be smaller.

Fig. 2 displays the phase diagram in the parameter space of t' and U with fixed $J/t = 0.5$ at the half filling. There are three distinct phases. The system is in the AFM phase at large U and small t', the paramagnetic metallic phase at small U and large t', and the SC phase at the intermediate parameter region. Here we have defined a paramagnetic metallic phase if $\Delta \le 0.01$. At this very small Δ, the energy difference between a SC state and a normal metallic state is practically indistinguishable. The phase boundary between the SC and normal states thus obtained is indicated by a dashed line [38]. For comparison, a schematic phase diagram abstracted from experimental measurements is shown at the right panel. Details of the pressure-temperature

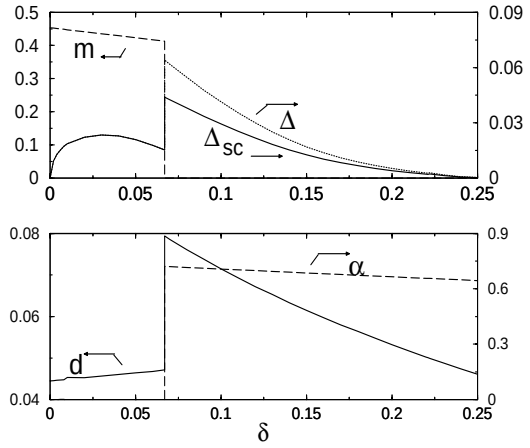

FIG. 3: Doping δ dependence of Δ, Δ_{SC} and m (top panel), and d and α (bottom panel) for $U/t = 8$, $J/t = 0.5$ and $t'/t = 0.8$.

phase diagram of the AFM insulating salt have been reported [7, 9, 10]. The effect of pressure in the schematic phase diagram is to decrease U/t or to increase t'/t. Our theory is consistent with the general features of this experimental phase diagram. Note that the t-U-J model does not represent the Hubbard model at small U. As it is well known, the ground state of the Hubbard model with $t' = 0$ at the half filling is an antiferromagnet. In our study of Eqn. (1), J is considered as an independent parameter, so that the J-term together with the kinetic term is in favor of a metallic state at $U = 0$ or small U/t.

Away from the half filling, similar calculations are conducted. The doping ($\delta = 1 - n$) dependences of various quantities are plotted in Fig. 3 for $U > U_c$. As δ increases from zero to a critical doping $\delta_c \approx 0.07$, the AFM order parameter m decreases slightly, and Δ_{SC} increases initially, then saturates. The ground state is an unprojected SDW and SC state ($\alpha = 0$), where the AFM and SC phases co-exist. At $\delta = \delta_c$, m drops to zero. The sudden disappearance of the AFM order strongly enhances the SC pairing. Δ_{SC} has a jump at $\delta = \delta_c$ followed by a slow decrease as δ further increases. In the region $\delta > \delta_c$, we have a pure d-wave SC state. The essential physics here is similar to the doped RVB state [26], except that here we have a strong first order phase transition on the AFM ordering at δ_c, a point which requires further study.

In summary, we have presented a strong coupling variational theory to examine the superconductivity near antiferromagnetic Mott insulator in layered organic conductors by using a Hubbard model including a spin-spin coupling term. The theory appears qualitatively consistent with a number of major experiments, such as the first order phase transition between AFM Mott insulator and superconductor under pressure, the merge of the metal-insulator transition and the AFM-SC transition point, the pseudogapped phenomenon in the SC state, the large magnetic moment in the AFM phase, and the transition to the normal metallic phase at high pressure. The present theory may be further improved by using variational Monte Carlo calculations on the expectation values and by developing a more accurate Hamiltonian-trial-wavefunction approach describing the physics of the layered organic conductors.

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